

SDMS Doc ID 165641

USING METAL PRELOADING AND CHEMICAL REGENERATION TO IMPROVE GAC PERCHLORATE ADSORPTION CAPACITY

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ABSTRACT

Perchlorate may be contaminating the water that 12 million Americans drinking, particularly in California and Nevada. In bench-scale research, the authors have capitalized on the full-scale granular activated carbon (GAC) infrastructure that is already installed at several of the water utilities who process perchlorate-tainted water. By tailoring GAC with ferric-oxalic acid preloading, a 33% improvement in the time to breakthrough of 18 ppb perchlorate has been achieved to treat the perchlorate-tainted groundwater from Redlands, CA. A chemical regeneration protocol that employed sodium borohydride was able to restore most of the perchlorate adsorption capacity, and this was achieved without displacing the activated carbon out of the carbon beds. Up to four cycles of water service and chemical regeneration have been achieved thus far.

INTRODUCTION AND BACKGROUND

The California Department of Health Services (CDHS) has adopted a provisional action level of 18 ppb for perchlorate. Perchlorate appears prominently in groundwaters from the Crafton-Redlands plume in Redlands and Riverside, CA (up to 140 ppb), in the Las Vegas Wash area, NV (up to 3,700 ppb), and near other sites where perchlorate has been manufactured. Relatively high perchlorate doses inhibit the normal function of the thyroid gland, and its effects at low dose exposures are not yet known.

We have proposed to concentrate and destroy perchlorate on GAC, because many of the water utilities who must deal with perchlorate-tainted groundwater already have installed GAC beds to remove trace organic compounds. These utilities include the City of Redlands, CA, City of Riverside, CA, and Las Vegas, NV. Thus, the technical approach herein is envisioned to control both perchlorate and organic contamination with essentially the same unit process. Likewise, it is also proposed to destroy the perchlorate through thermal reactivation, because several water utilities who use GAC already thermally reactivate their GAC when it has become

exhausted in its organics adsorption capacity. For example, the City of Redlands practices thermal reactivation. Thus, it has been proposed herein to capitalize on the infrastructure and operations knowledge that water utilities already have to achieve a relatively inexpensive method for also removing and destroying perchlorate.

Various methods have been described in the literature for reducing and destroying perchlorate; and many of these were initially developed for monitoring perchlorate by titrimetric redox methods. These reduction reactions generally require a catalyst or high temperature (Lamb and Marden,1912; Lenher and Tosterud 1922; Dobroserdov and Erdmann,1926, 1927; Yamasaki et al., 1973 and 1974; Crump and Johnson, 1955; Meldrum et al.,1948; Scharrer,1926; Groh and Neumeister, 1926). Perchlorate has been used as an aggressively reactive oxidizer when coupled with solid rocket fuel at high temperatures. Because of its limited shelf life, it had to be periodically washed out of the country's missile and rocket inventory and replaced with a fresh supply. Thus, large volumes of the compound have been disposed of in California, Nevada, and other states since the 1950's. At ambient temperature, perchlorate remains kinetically stable for long durations when it is dissolved in natural waters at concentrations up to 1,000 mg/L (AWWA, 1997). However, it is thermodynamically unstable and very reactive at high temperatures. Hence, by employing thermal reactivation at high temperatures to ultimately destroy perchlorate, municipalities can put to good use the highly reactive feature about perchlorate caused it to be used in rocket propulsion in the first place.

Numerous wet chemical and electrochemical methods for reducing perchlorate to chlorine or to chloride at ambient temperature have also been described, but most of these involve precious or heavy metals, unusually low pH levels, or complicated combinations of electrodes and membranes. These generally appear to be beyond the scope, cost constraints, time constraints, operational constraints, and feasibility of water utilities.

The physical-chemical methods for removing and destroying perchlorate have been targeted, because the water industry primarily relies on physical-chemical methods to treat their water. In contrast, many water utilities have neither the infrastructure, technical background, nor desire to employ biological methods; and for good reason. Any biological treatment process creates both "helpful" and "unhealthful" microorganisms, and the microorganisms must therefore be filtered and disinfected from a water supply before a biologically-treated water can be

purveyed to customers. Such post-treatment is required by law in many states, including California.

City of Redlands, CA Experience with GAC and Perchlorate Removal: The City of Redlands hosts its Texas Street water treatment plant, which has been equipped with 24 GAC contactor vessels (or 12 pairs of vessels). This GAC facility was initially installed to remove trichloroethylene (TCE-a solvent) and dibromochloropropane (DBCP-a pesticide) from a groundwater plume. Each pair of two vessels together contain 40,000 pounds of GAC, and they were designed to together provide a 40 minute empty bed contact time (EBCT) in each vessel pair at 4.3 MGD, or 30 minute EBCT at 6.5 MGD, or 20 minute EBCT at 8.6 MGD. These have been operated with two vessels in series, such that at any given time 12 vessels are in the "lead" mode, and 12 are in "follow" mode. As conventionally operated for TCE and DBCP removal, when the organic contaminants penetrated half way through the "follow" vessel, the "lead" vessel was taken out of service and regenerated. At this time, this "follow" vessel became the new "lead" vessel, and a new "follow" vessel commenced service down stream of it. On the basis of organic loading parameters, the Redlands staffs have been taking a GAC vessel out for thermal reactivation after it has been in operation for 18 months while operating at roughly 4.3 MGD. Reactivation of this bituminous GAC (Westates Northwerstern LB 830) has been performed off site by U. S. Filter Westates.

The Texas Street plant has been treating water from Well 31A, which can deliver 4.3 MGD, and is one of Redland's higher-yielding wells. This groundwater originates from within the Crafton-Redlands plume area; and in addition to the TCE and DBCP, this groundwater also contains 60-138 ppb perchlorate. Once perchlorate was detected in this well, the Texas Street plant was shut down. The City of Redlands also has two other wells (30A and 32) that can deliver water through the Texas Street plant; and well 32 samples contained 20-50 ppb perchlorate. After isolating high-nitrate water tables from the upper levels of these two well screens, wells 30A and 32 are expected to deliver 2.3 MGD; and thus the projected capacity for the Texas Street plant will ultimately be 6.5 MGD. Redlands also has other groundwater and surface water sources that contain scant perchlorate. In the summer, Redland's peak day water demands of 45-50 MGD are just matched by their system-wide water treatment capacity; and water production at Texas Street will soon become crucial for meeting these summer demands.

The City of Redlands conducted testing regarding perchlorate removal by full-scale GAC vessels that commenced operation on May 5, 1997 and remained in service through a sampling event on June 3, 1997. During this month, the flow averaged 3.6 MGD through their 12 pairs of vessels, and the flow was 4.3 MGD on June 3, which corresponded to a 40-minute EBCT through two vessels in series. During May 5- June 3, there had been 93 MG of water that had processed through the Texas Street GAC beds, and there had been 730 skid-bed volumes (i.e. the volume of both beds in a skid together) processed through vessels 1A and 1B together. During most of the operations time, groundwater originated from Redland's Well 31A, which was analyzed to contain 62-138 ppb perchlorate.

On June 3, 1997, water was sampled from Vessels 1A and 1B at eight port locations, with resultant perchlorate concentrations as shown in Table 1. This table highlights that the GAC confined its perchlorate mass transfer zone within 15-20 minutes. The data also shows that when these GAC vessels were operating in the above-described mode, they could have processed roughly 1280 skid-bed volumes of groundwater before 18 ppb perchlorate would have broken through, and they would be 80-85% exhausted at 2560 skid-bed volumes, or twice the bed volumes to 18 ppb threshold. This would correspond to six weeks of operation until change-out of a given single "lead" bed, with a 40 minute empty bed contact time (EBCT) through the two beds together.

This three weeks of operation between change-outs, as required by perchlorate loading, would be short relative to the 18 months between change outs as required relative to organic loading requirements. None-the-less, the authors emphasize that this currently available commercial GAC was indeed effective at removing perchlorate. It just was not effective for very long, nor for as low a cost as for other conventional water treatment operations that are designed to remove other contaminants (such as turbidity, etc.). The intent of the research herein has been to build on this finite adsorptive capacity, move beyond what has previously been available commercially, and to tailor a GAC and interim chemical regeneration protocol that would translate an effective but expensive technology into an effective and inexpensive technology.

Table 1. Perchlorate Removal through City of Redlands GAC Vessels on June 3, 1997, following Start-up on May 5, 1997

Sample Port	Cumulative Empty Bed Contact Time, min ⁺	ClO ₄ -, ppb	Relative ClO ₄ , ppb	Bed Volumes Processed above This Sample Port
1/8	5	101	0.92	5840
1/4	10	97	0.88	2920
3/8	15	87	0.79	1950
1/2	20	39	0.35	1460
5/8	25	5	0.05	1170
3/4	30	0	0.00	980
7/8	35	0	0.00	840
1	40	0	0.00	730

The first 4 ports are in Vessel 1A; the other 4 ports are in Vessel 1B.

MATERIALS AND METHODS

The Rapid Small-scale Column Tests (RSSCT): As well known, mass transfer mechanisms are very important in GAC adsorption. In order to simulate the influence of these mechanisms, the rapid small-scale column test (RSSCT) method has been employed. When the internal mass transfer controls, based on the dispersed-flow pore-surface-diffusion model, RSSCT provides two kinds of simulation according to different relationship of grain size and intraparticle diffusion: the constant diffusivity method and the proportional diffusivity method (Crittenden et al., 1983, 1987a, 1987b). The scale-down equations are presented as follow.

(1) Constant Diffusivity

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left| \frac{R_{SC}}{R_{LC}} \right|^2 \dots (1)$$

$$\frac{v_{SC}}{v_{LC}} = \frac{R_{LC}}{R_{SC}} \bullet \frac{\text{Re}_{SC,\text{min}}}{\text{Re}_{LC}}$$
 (2)

(2) Proportional Diffusivity

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left| \frac{R_{SC}}{R_{LC}} \right| \tag{3}$$

⁺ Skid-bed volumes based on 93.11 MG total water processed from May 5th to June 3rd, 1997; and 1.1 times as much flow rate through Vessels 1A&B than was averaged through all.

$$\frac{v_{sc}}{v_{lc}} = \frac{R_{lc}}{R_{sc}} \bullet \frac{\text{Re}_{sc,\text{min}}}{\text{Re}_{lc}}$$
 (4)

where EBCT =empty bed contact time

SC = small column

LC = large column

R = carbon grain radius

v = flow rate or velocity

Re = Reynolds number,

Remin.sc = the minimum Reynolds number that can be used in the small scale column

To decide which scale-down method should be used, the breakthrough curves of full-scale beds and RSSCT beds must be compared. While for many organic contaminants, many comparisons have already been done, the comparison for perchlorate was performed in this research.

Because of the lack of full operation data, the full-scale breakthrough curve was created from the column profile based on the perchlorate concentration obtained at eight sampling points as presented previously. This method may overestimate the adsorption capacity to some extent. The simulated EBCT was 20 minutes and the simulated flow rate was 4.3 MGD. These data represent either the "lead" or "follow" bed in Skid 1 (1A or 1B). Therefore, not only the 18-ppb CDHS provisional action level but also the complete adsorption capacity of perchlorate should be analyzed. The 80% breakthrough was used as the representative of the adsorption capacity. According to the curve (see Figure 1.), the 80% breakthrough for perchlorate adsorption is about 2,560 bed volumes. This compares with the breakthrough for organic contamination adsorption of about 33,000 bed volumes, or 18 months operation.

The RSSCT simulation beds were calculated according to the equations presented previously. The small-scale carbon grain size was always of the diameter of 1190 μ m (600 μ m~2360 μ m, U.S. mesh 60×80). All of the carbons were seived, washed and dried at 105 °C for 24 hours before using. Re_{SC,min} used in Equations (2) and (4) was selected as 0.13 due to the recommendation of 0.13 for the simulation of the organic contaminants of 100-300 Dalton in water solution and the consideration that hydrated perchlorate anions are very small. For the

constant diffusivity method, the RSSCT column length was 1 cm with the EBCT of 0.63 minutes. For the proportional diffusivity method, the RSSCT column length was 13.1 cm with the EBCT of 3.56 minutes. The cross-section diameter of RSSCT columns was selected under the consideration of channeling effects. As recommended by the RSSCT method, it must be at least 50 times of the grain size. The diameters used were 1.25 cm and 1.38 cm. Although some RSSCTs were made with the column length of 13.1 cm, most of them were made with certain amount of GAC. The GAC mass was decided by multiplying the column volume with the carbon apparent density, which was 500 mg/L as estimated in the full-scale beds. It turned out that by using, a pre-designed certain amount of GAC, it was impossible to achieve the column length of 13.1 cm, i.e., the apparent density within the RSSCT column was lower than for the full-scale bed. However, for the sake of comparison, all the water processed was converted to bed volumes by dividing the water volume by the column volume as if its length had been of 13.1 cm with equal apparent density to full-scale bed, even though the real length was longer than 13.1 cm (i.e. 15 or 18 cm with lower apparent density).

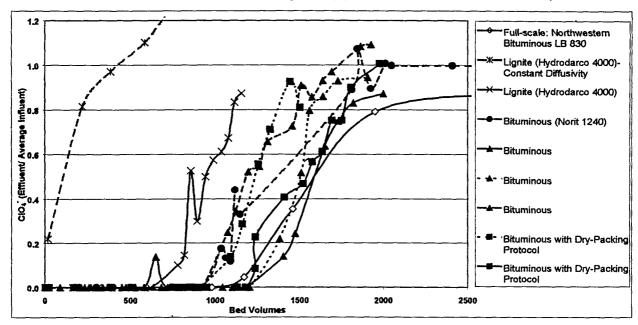
A transparent chemical-resistant plastic pipe was used to make the RSSCT columns. GAC was packed inside the pipe and stopped by glass wool at each end. Two different packing protocols were conducted. One was the wet-packing protocol with which GAC was wetted by DI water before it was poured into the column, the other was the dry-packing protocol without wetting. The packed column was set upright with the inlet end at the bottom. Non-coagulated groundwater from Well 31 A Texas Street, Redlands, CA was pumped through chemical-resistant tubing. Most of the water had a perchlorate level of 70~80 ppb. At each sampling time, samples were taken both from before the column as influent and after the column as effluent. The relative effluent concentrations were obtained by dividing each effluent concentration by the average influent concentration. The perchlorate concentration was analyzed by DIONEX DX 500 ion chromatography. With the recommended method and column, this unit could detect a perchlorate level as low as 4 ppb (Wirt, K. et al. 1998). The comparison of RSSCT simulation and full-scale performance is shown in Figure 1 as follows, and the complete RSSCT column settings are shown in Table 2.

According to Figure 1., it is apparent that the proportional diffusivity simulation was much more suitable than the constant one, and the simulation using bituminous carbons was better than that using lignite carbon. The best simulation breakthrough curves using SAI 6080

bituminous carbon matched nearly identically with the full-scale breakthrough curve as inferred from a single-date profile (Table 1.).

Figure 1. Comparison of Full-Scale Performance as Inferred from Single-Date Profile versus RSSCT Breakthrough Curves

(All RSSCT columns scaled for proportional diffusivity, unless otherwise listed; all SAI 6080 unless otherwise listed; all wet packing protocol unless otherwise listed.)



Preloading Methods: One of the strategies used to increase the perchlorate adsorption capacity was to preload GAC with metal-oxalic acid complexes. The metal salts included iron (FeCl₃), manganese (MnCl₂·4H₂O), aluminum (Al₂(SO4)₃·18H₂O), magnesium (MgSO₄·7H₂O) and calcium (CaCl₂·2H₂O). Most tests employed the iron salt. These metals were selected because there are no primary drinking water regulations associated with them. Certain amounts of one of these chemicals and oxalic acid were poured into a 4-litre bottle with 30 grams of GAC and mixed in 2 L deionized (DI) water. Then, the filled bottle was sealed and placed on a shaker table and shaked for 48 hours at good mixing conditions. After 48 hours, the carbon was briefly washed by DI water and dried at 105 °C for 24 hours. After drying, the carbon was sieved through 60×80 mesh and briefly washed by DI water again to remove carbon fines. Then after another 24-hour period of dehydration, the carbon mass was monitored. The parameters

pertaining to the RSSCT columns, including both preloaded and unpreloaded, are listed in Table 2.

Table 2. Preloading Conditions and Column Parameters

				Preloading*							
Group	RSSCT /Full- Scale [†]	GAC ⁺⁺	Carbon Mass ⁺ (g)	Metal (mM)		Ratio of Metal and Oxalic Acid (mM:mM)	Column Length** (cm)	EBCT (min)	Diameter	Rate	Packing Protocol (dry/wet)
	F	N	9060K				244	20	300	0.213	
	С	Н					1.0	0.63	1.25	0.028	Wet
	P	Н					13.1	3.56	1.25	0.061	Wet
	P	No					13.1	3.56	1.25	0.061	Wet
	P	S		38.4	27.7	1.39	13.1	3.56	1.25	0.061	Wet
	P	S	9.8				15.0	3.56	1.25	0.061	Dry
1	P	Ş	9.8	 8.93 Fe 2.98 Fe 17.86 Fe	6.44 2.15 12.88	1.39	18.0	3.56	1.38	0.061	Wet
2	P	S	9.8	8.93 Fe 2.98 Fe 17.86 Fe	6.44 2.15 12.88	1.39	18.0	3.56	1.38	0.061	Wet
3		S	9.8								
	P			8.93 Fe	17.86 8.93 4.47 2.24 0.89	0.5 1.0 2.0 4.0 10.0	18.0	3.56	1.38	0.061	Wet
4	P	S	9.8	9 Mn 9 Al 9 Mg 9 Ca	6.44	1.39	15.0	3.56	1.38	0.061	Dry

^{*} F=Full-Scale; C=constant-diffusivity RSSCT; P=proportional-diffusivity RSSCT

The lengths were approximate.

^{**} N=bituminous Northwestern; H=lignite Hydrodarco 4000; No=bituminous Norit 1240; S=bituminous SAI 6080

^{*} The chemicals used were Oxalic Acid ((COOH)₂·2H₂O), FeCl₃, MnCl₂·4H₂O,

Al₂(SO₄)₃·18H₂O, MgSO₄·7H₂O and CaCl₂·2H₂O.

Chemical Regeneration: The other strategy used to increase the perchlorate adsorption capacity was chemically regeneration of the perchlorate-exhausted GAC by sodium borohydride. The regeneration was conducted by passing a NaBH₄ solution (100 mg/L, unless otherwise listed) through an exhausted column at the same flow rate as for perchlorate loading. The effluent perchlorate concentration was sampled periodically. After regeneration, some columns were loaded again to examine the cyclically repeated performance of chemically regenerated GAC.

RESULTS AND DISCUSSIONS

Groups 1 and 2 experiments were conducted to test how different iron-oxalic acid preloading conditions affected perchlorate adsorption. The results are presented in Figures 2 and 3, respectively. Both groups of tests revealed that at the intermediate iron and oxalic acid preloading conditions, the perchlorate adsorption was the best; and this was better than that of the unpreloaded carbon. Overdosing or underdosing the iron and oxalic acid preloading did not improve perchlorate removal much, or even reduced the perchlorate adsorption capacity.

One possible mechanism of the improvement may be that the iron-oxalic acid complexes induces positive electric charges onto GAC grains, making it more polar and improving its capacity of extracting perchlorate from water. However, overloading may block the GAC pores and hence decrease its adsorption capacity.

The ferric iron concentration in Group 3 was fixed at 8.93 mM and the oxalic acid concentration was varied from low to high relative proportions. These results are presented in Figure 4. As shown in the Figure, when the oxalic acid concentration was 8.93 mM and 8.93 mM, the perchlorate adsorption was improved the most. Even at other oxalic acid concentrations, the preloading still improved the perchlorate adsorption capacity dramatically.

If the CDHS provisional action level of 18 ppb is chosen as the criterion, the unpreloaded SAI 6080 RSSCT columns in Groups 1, 2 and 3 broke through at 1476 BVs, 1390 BVs and 1070 BVs, respectively. The first two columns were packed with the wet-packing protocol while the third one was packed with the dry-packing protocol. The difference of about 300 BVs might be caused by the different column length achieved by these two different packing protocols. At 18 ppb, the best performed columns in these groups broke through to 18 ppb at 1546 BVs, 1450

BVs and 1420 BVs, which represented 5%, 4% and 33% improvements, respectively. These data are listed in Table 3 as follows. Table 3. Also lists % improvement in Bed Volumes to 80% breakthrough.

Figure 2. Influence of Ferric-Oxalic Acid Preloading on Perchlorate Removal from Redlands Groundwater (Group 1)

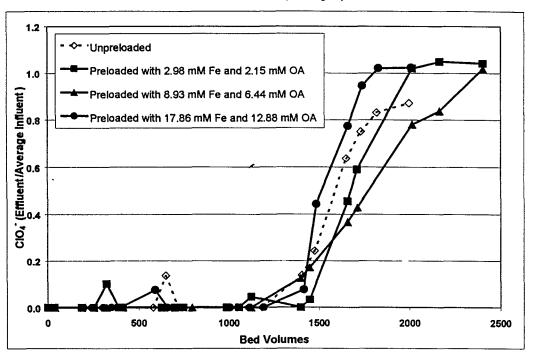


Table 3. Improvement of Perchlorate Adsorption by Ferric-Oxalic Acid (Criterion = 18 ppb CDHS Provisional Action Level)

	Breakthrough of	Best Preloaded	Performance	Improvement	Improvement	
Group	the unpreloaded GAC to 18ppb BV	Preloading	Preloading Breakthrough BV		% to 80% breakthrough	
1	1476	8.93 mM Fe; 6.44 mM Oxalic Acid	1546	5	16	
2	1390	8.93 mM Fe; 6.44 mM Oxalic Acid	1450	4	9	
3	1070	8.93 mM Fe; 8.93 mM Oxalic Acid	1420	33	16	

Figure 3. Influence of Ferric-Oxalic Acid Preloading on Perchlorate Removal from Redlands Groundwater (Group 2)

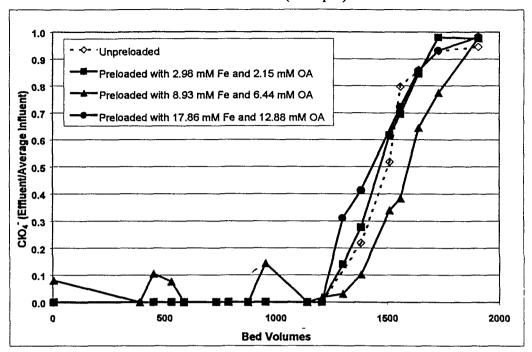
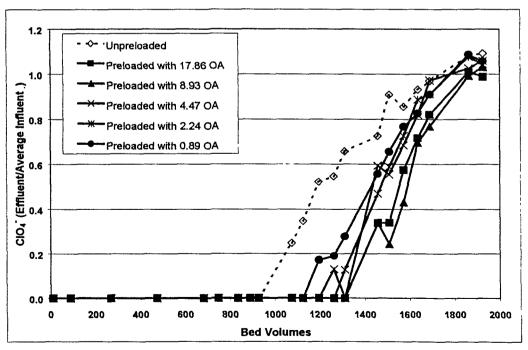
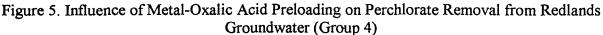


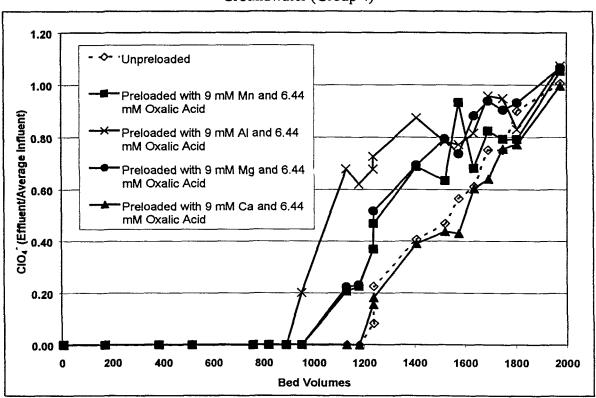
Figure 4. Influence of Ferric-Oxalic Acid Preloading on Perchlorate Removal from Redlands Groundwater (Group 3, Fe = 8.93 mM)



The metal-oxalic acid preloadings other than ferric-oxalic acid were tested in Group 4. These results are presented in Figure 5. According to this figure, the preloading with Ca-oxalic acid complexes increased the perchlorate adsortion capacity slightly while other preloadings diminished the perchlorate adsorption. However, to make definitive conclusions relative to these matals, further research is needed, especially for the Ca-oxalic acid preloading.

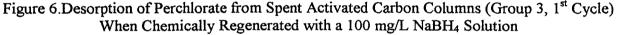
As shown as in Figure 6, the perchlorate desorption behavior was quite distinct, and it was characterized by a long lag time before the perchlorate commenced to exit the GAC columns. This was quite a different behavior than would commonly be observed for an organic compound, which would generally commence desorbing right away. The cause of the perchlorate desorption behavior warrants further study and explanation. It is possible that both the activated carbon surface and the perchlorate are reduced by the sodium borohydride, and the desorption/destruction impact on the perchlorate is not manifest until a redox threshold pertaining to the activated carbon is exceeded.





It is also noteworthy that the ferric-oxalic acid preloading conditions that achieved the greatest enhancement in perchlorate removal were also the conditions that exhibited the longest delay during chemical regeneration until the perchlorate was released. Specifically, the activated carbon column that was preloaded with 8.93 mM Fe and 8.93 mM oxalic acid was the one that exhibited the greatest perchlorate removal capacity, and this column was also the one that exhibited the longest delay until perchlorate was released during chemical regeneration, with a peak appearing after 70 bed volumes of sodium borohydride solution.

Two of these regenerated columns were loaded again. The comparison of their performances in the first and second cycles is presented in Figure 7. The results show that much of the original perchlorate adsorption capacity was restored following chemical regeneration. Specifically, during the second cycles, a 18 ppb perchlorate breakthrough occurred after the columns in their second cycles had processed 1000 bed volumes of Redlands groundwater, as compared to 1300 bed volumes in the first cycle. Bed volumes to 80% breakthrough were the same for the chemically regenerated GAC beds as they had been for the virgin GAC beds.



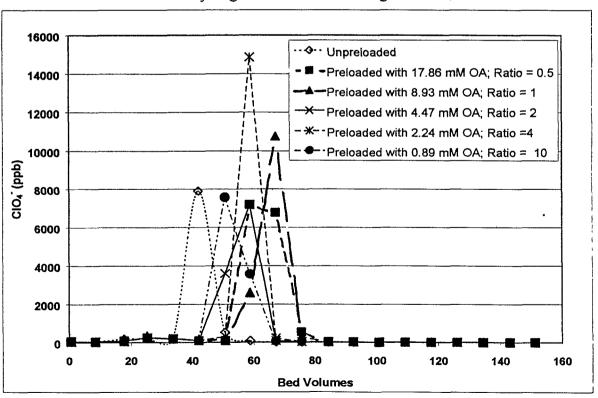


Figure 7. Perchlorate Adsorption Capacity following Chemical Regeneration: Comparison of First Cycle to Second Cycle for Activated Carbon that was Preloaded with Ferric-Oxalic Acid; and Chemically Regenerated with 100 mg/L NaBH₄ following the First Adsorption Cycle

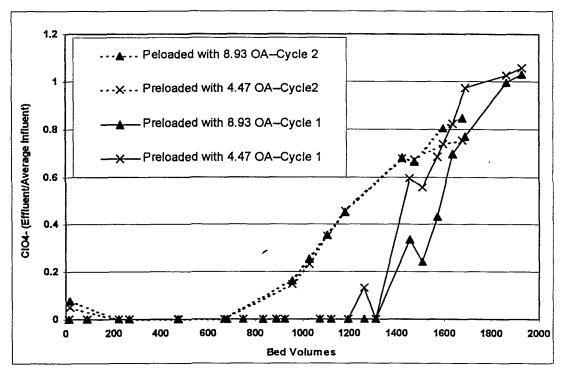
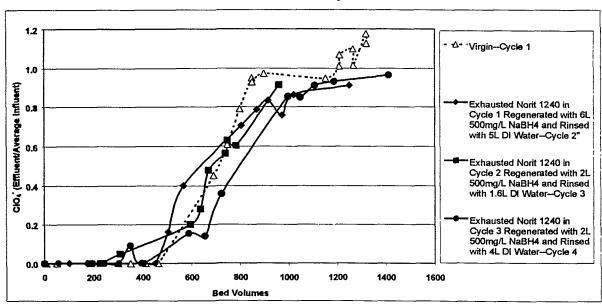


Figure 8. Perchlorate Adsorption Capacity Following Chemical Regeneration: Comparison of First, Second, Third and Fourth Cycles for Norit 1240 That Was Preloaded 38.4 mM Ferric Iron and 27.7 mM Oxalic Acid; and Chemically Regenerated with NaBH₄

After Each Cycle



Another comparison of virgin and spent activated carbons is presented in Figure 8. The perchlorate adsorption capacity of bituminous Norit 1240 that had been preloaded with 38.4 mM ferric iron and 27.7 mM oxalic acid could be completely resumed even after three cycles of chemical regeneration.

SUMMARY AND CONCLUSIONS

Using ferric-oxalic acid preloading to improve the perchlorate adsorption is promising. The bitumious SAI 6080 preloaded with 8.93 mM ferric iron and 8.93 mM oxalic acid could improve the perchlorate adsorption from the Redlands groundwater to about 33% compared with the virgin activated carbon, when measured as bed volumes to 18 ppb perchlorate break through. When combined with the chemical regeneration using sodium borohydride, the activated carbon might be able to stay in service for perchlorate adsorption as long as for organic removal. This, in turn, would provide the opportunity for the complete perchlorate destruction by thermal regeneration or other methods after several cycles of chemical regeneration.

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